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Labile and Refractory Organic Nitrogen in Chesapeake Bay Wastewater Treatment Plants : Measurement and Model Simulation

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Introduction

Labile and refractory organic nitrogen are arbitrary splits of organic nitrogen compounds, which are differentiated essentially by the length of time required for decay. Labile and refractory organics include both dissolved and particulate forms. The process of decay, mineralization, or diagenesis* of organic nitrogen to the bioavailable forms of dissolved inorganic nitrogen (ammonia and nitrate) often takes the form of relatively high mineralization rates over hours to days, followed by a slower decay rate over years to decades depending on microbial activity and opportunities for photooxidation. Diagenesis of organic nitrogen compounds is also called ammonification, as ammonia is a product of the organic nitrogen decay process.

Labile and refractory organics are empirically defined. For water quality models a working definition usually suffices. For example if a watershed model domain has flows of several days to weeks before discharge of an organic nitrogen load, a BOD₅ would be a useful split between what would decay within the simulation period, or the labile portion of organic nitrogen, and what would remain inert within the model domain, the refractory portion.

On the other hand, an estuarine model with detention times of dissolved materials of weeks to months and detention times of particulate material of years to decades, would want to have a split of labile and refractory organic nitrogen based on something like a BOD_{ultimate} or equivalent, with whatever fraction left undecayed considered refractory, but still given a very slow reaction rate. The approach used in the sediment diagenesis component of the Chesapeake Bay Water Quality Model is to have several rates of organic decay including a fast labile rate of several days, a fast refractory rate of weeks to months, and a remaining refractory portion that has a slow decay rate occurring over years. In all cases, fast labile, fast refractory, and refractory, there is continuing decay to inorganic nitrogen. The only difference is the rate.

*Note: Throughout this manuscript the terms diagenesis, mineralization, and oxidation of organics are used interchangeably, all describing the decay of organic nitrogen to inorganic forms.

Measurement of organic labile and refractory concentrations relies on some measure of the rate of decay or diagenesis. These include measures of Biochemical Oxygen Demand over five days (BOD_5), twenty days (BOD_{20}), and ultimate biochemical oxygen demand ($BOD_{ultimate}$) (Metcalf and Eddy, 1979; Salvato, 1982)). There are also different measures of bioavailability of organic nitrogen in the literature (Seitzinger and Sanders, 1997; Seitzinger et al., 1996). These measures give an indication of the amount of organic carbon, nitrogen, or phosphorus that have decayed over a period of time. In a sense, the method of measure becomes the definition of labile and refractory split. If a BOD_5 was used, then the portion of organic material decayed in five days would be considered labile and the portion of organic nitrogen remaining would be considered refractory. The same approach would be applied for the case of labile and refractory splits based on BOD_{20} and other longer decay experiment methods. The relationship among the labile/refractory definitions, the unit of measure of the labile and refractory portions, and the residence time of the water body are important considerations.

Literature on Labile and Refractory Nitrogen in Rivers, Estuaries, and the Coastal Ocean

There is a long-standing and growing body of literature on the ultimate fate of organic nitrogen ranging from classic measurements of BOD_5 , to more recent measures of labile and refractory organic nitrogen bioavailability over short and long periods. Experiments by Seitzinger and Sanders (1997) using 10 to 15 day decay experimental methods on river dissolved organic nitrogen (DON) from the Delaware and Hudson Rivers found the “average DON concentrations decreased by 40 to 72% within the 10 to 15 day time course of the experiment; the decreases were accounted for by increases in microbial biomass plus remineralization to inorganic nitrogen”. In the development of their paper they look at rate of decay as an indication of the likelihood that diagenesis would occur in the river, estuary, or coastal ocean. Estuaries with a higher portion of refractory nitrogen inputs combined with low estuarine retention times would tend to move the decay of organic nitrogen to coastal waters. They further point out that the labile and refractory forms of nitrogen also have dissolved and particulate forms, and that, “the dissolved forms are most likely to be immediately available to planktonic microorganisms. Bacteria and some phytoplankton rapidly assimilate very low molecular weight compounds such as amino acids and urea (e.g. Wheeler and Kirchman, 1986; Fuhrman, 1990; Antia et al., 1991; Gilbert et al. 1991; Keil and Kirchman, 1991; Cotner and Gardener, 1993; Tranvik, 1993)”.

Dissolved organic nitrogen in most regions of the Chesapeake would have a detention time of several months. Residence times of water, estimated by an “age of water” model analysis, are on the order of three to four months for waters in the upper Bay (CB1TF) or the tidal fresh Potomac (POTTF) (Wang, 2003). Waters of the lower Chesapeake tributaries, such as the headwaters of the York, have residence times of about two months. The age of water analysis estimate, is based on hydrodynamic modeling of the Chesapeake using a Lagrangian subroutine to track a particular water source within a larger Eulerian hydrodynamic simulation. The Chesapeake retention times of dissolved organic nitrogen is a longer course of time than the length of any decay experiments found in the literature. If oxidation of dissolved organic nitrogen does not occur in the watershed or estuary, the possibility of further oxidation in coastal shelf waters is likely, at least at some slow rate. Long time courses, and the different forms of oxidation of organic material, including microbial and photooxidation, must be taken into account.

Particulate organic nitrogen is likely to be retained within the estuary as determined by model

tracer experiments of conservative particulate tracers (Linker and Neumiller, 1994). The particulate nitrogen, after settling to the bottom, begins a long process of decay (DiToro, 2001; DiToro and Fitzpatrick, 1993). From DiToro (2001, page 17), Figure 1 shows the decay of organic carbon and organic nitrogen in Chesapeake Bay sediment cores. The data, taken from Schubel and Hirschberg (1977), shows the decay over thirty centimeters of sediment cores taken from the Chesapeake. There is a ten to one ratio of organic carbon to organic nitrogen due to stoichiometric mass considerations. The straight lines plotted on log scale through the data indicate the rate of decay is slowing with increasing core depth or age, but continues. The other item of note is that this slowing rate of decay is going on for 30 centimeters of core. The sedimentation rate represented by these cores is typical for the Chesapeake and is estimated to be on the order of 0.25 cm/yr. In other words, the rate of decay of organic nitrogen has slowed over 120 years, but not stopped. Assuming a sedimentation rate of 0.25 cm/yr, this corresponds to a decay rate of 0.014 yr^{-1} or a half life of 50 years - a slow, but steady rate of mineralization to dissolved inorganic nitrogen forms. Overall, the organic nitrogen in the surface layers to the bottom of the 30 cm core have decreased by about an order of magnitude, from 0.3% of sediment composition at the surface to 0.05% at 30 cm of core depth.

Further evidence that the rate of mineralization is a constant, albeit slow, process for the more refractory forms of organic nitrogen is the absence of any known pools of organic nitrogen in the water column or sediment. Seitzinger et al. (1996) examined a large pool of dissolved organic nitrogen from the ocean as a load imported to the Chesapeake from coastal shelf waters. Her group found that "dissolved organic nitrogen (DON) comprises a major portion (65% to 75%) of the total nitrogen in surface and bottom water at the mouth of the Chesapeake Bay and in coastal ocean water." The team found that substantial portions of the DON was labile, and that rates of utilization (uptake by algae) ranged from 2% to 5% day^{-1} . Algal utilization experiments and long-term decay experiments lasting as long as fifty days were conducted.

The above review of the literature shows that much depends on the boundaries of the problem. For watersheds the critical period of time is days to about a week. Organic nitrogen oxidizing in this time period considered to be labile or reactive with respect to the boundaries of the watershed. For estuaries, much depends of the retention time for organic nitrogen, with the Chesapeake having relatively long detention times for dissolved organic nitrogen of up to four months. Most all the particulate organic carbon is likely to be retained in the Chesapeake and the ultimate fate of organic nitrogen in Chesapeake sediment, except for a very refractory 1% to 2%, is that of diagenesis at rates at first fast, and then slowing as burial and time passes. Detention times of organic nitrogen in coastal shelf waters are unknown but estimates of months to years are not unreasonable. This provides a long period for both microbial and photooxidation of organics in the combined Chesapeake watershed, estuary, and coastal waters.

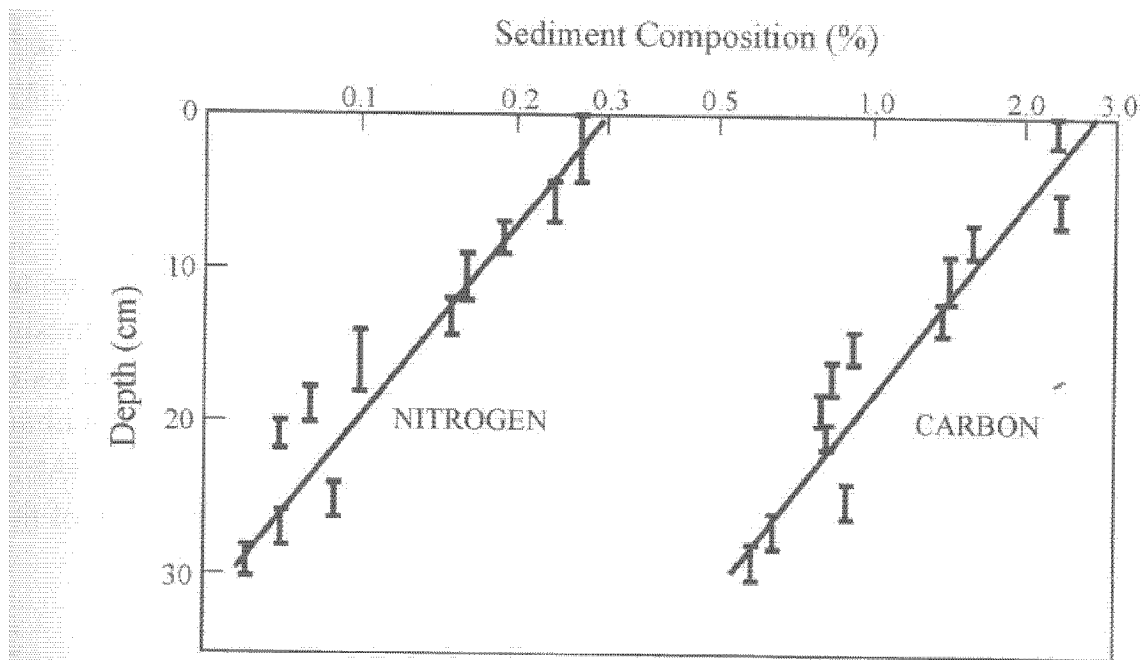


Figure 1. Logarithm of the organic carbon and nitrogen concentration versus depth in a sediment core. Data from Schubel and Hirschberg (1997).

Source: *DiToro Sediment Flux Modeling*, 2001

Measurements of Labile and Refractory Organic Nitrogen

Measurement of labile and refractory portions of organic nitrogen are estimated by Biochemical Oxygen Demand (BOD) methods of specified periods such as 5 days (BOD_5), 20 days (BOD_{20}) or by chemical oxidation ($BOD_{ultimate}$) (Metcalf and eddy; Salvato 1992). Long term decay, and algal uptake methods are used as well (Seitzinger and Sanders; 1997; Seitzinger et al. 1996).

The BOD_5 method is the most common method of estimating the portions of labile and refractory organics. Being able to distinguish between estimates of a 5 day labile and a refractory beyond five day split of organic nitrogen, the BOD_5 method is often used for judging the immediate oxygen demand of an organic discharge and likelihood of mineralization within river systems. The method involves incubation of the organic material in solution for a five day period at a temperature of 20° C. As Metcalf and Eddy (1972) relate, “Biochemical oxidation is a slow process and theoretically takes an infinite time to go to completion. Within a twenty day period, the oxidation is about 95 to 99% complete, and in the 5 day period used for the BOD test, oxidation is from 60 to 70 percent complete. The 20° C temperature is an average value for slow moving streams in temperate climates and is easily duplicated in the incubator.”

The BOD_{20} method uses a twenty day incubation period to allow for the further oxidation of ammonia to nitrate (nitrification) and is often called second-stage BOD.

The $BOD_{ultimate}$ is a measure of the BOD mineralized over a theoretical infinite period of time

(Salvato, 1982) representing complete mineralization. Relationships among BOD_5 , BOD_{20} , and $BOD_{ultimate}$ well known and equations for relating one to the other are fully developed in Metcalf and Eddy (1972).

Simulation of Organic Nitrogen in Chesapeake Bay Models

In the Chesapeake Bay models of the watershed and the estuary organic nitrogen is usually derived from defaults as described in Table 1. The splits of organic nitrogen are updated on a regular basis to reflect changing treatment technologies.

The Chesapeake Water Quality and Sediment Transport Model (WQSTM) further splits the organics into a dissolved and particulate fraction of 50/50 for organic nitrogen and 40/60 for organic phosphorus based on the average measured effluent of seven dischargers (Cercio and Noel, 2002). The particulate organic fraction is further divided into labile and refractory portions of 15/85 for organic nitrogen and 7/93 for phosphorus (Cercio and Noel, 2002). In the WQSTM the dissolved, particulate labile, and particulate refractory organic nitrogen portions all have reaction rates which are 0.025 d^{-1} , 0.12 d^{-1} , and 0.005 d^{-1} respectively. The simulation's assignment of reaction rates to all portions of organic nitrogen effluent discharging to the estuary is consistent with the long estuarine detention times. Equations for the different water column organic fractions are described in Appendix A.

In the sediment the organics are split into different fractions of relative reactivity called G1, G2, and G3. Each of these organic nitrogen fractions also have a reaction rate with G1, the relatively freshly deposited sediment organic fraction, having a reaction rate of 0.35 d^{-1} . The sediment organic fraction with an intermediate reactivity is G2 with a reaction rate of 0.0018 d^{-1} . The largely inert G3 fraction has a slow reaction rate of $6.8 \times 10^{-5}\text{ d}^{-1}$, consistent with a half life of 27.7 years.

The simulation of organic nitrogen in the Watershed Model takes a different approach based on the shorter retention times of rivers. The longest detention within Chesapeake rivers is on the order of about six days. As a consequence the Watershed Model refractory reaction rate is set to zero and refractory nitrogen is assumed to be inert in the Watershed domain. Once tidal waters are reached to longer detention times of the estuary hold sway and the estimated refractory organic nitrogen loads of the watershed model are transferred as a refractory input to the WQSTM which applies a rate of 0.12 d^{-1} to these loads. The shallow and varying depths between riffle and pool and the advective nature of rivers make the distinction between dissolved and particulate organics less important and so all the labile and refractory organics have a settling rate which is set for each river reach segment.

Table 1. Organic nitrogen and phosphorus species splits used for the Watershed Model and the Water Quality Sediment Transport Model.

+Apply this relationship wherever NH3 limits apply

Type of Point Source		NH3/NO3/OrgN (w/o Nitrification)	NH3/NO3/OrgN (w/ Nitrification)+	NH3/NO3/OrgN (w/Denitrification)
Municipalities		80/3/17**	7/80/13**	12/73/15
Industries	Chemical	7/85/8++		
	Pulp & Paper	1/0/99**		
	Poultry Facilities w/ BNR			8/75/17**
	Nonchemical (includes seafood, poultry, & food processors w/out BNR)	80/3/17**	7/85/8+	8/75/17**

++Assumed by performing an analysis of MD chemical industry wastewater effluents which showed it is very close to the relationship for nitrifying sewage. This would apply to all chemical discharges and assumes that wastewaters are treated chemically and thus would not vary as for sewage relationships

** Updated, as based on an analysis of actual data from plants operating in Virginia.

Conclusions

Reaction rates for labile organic nitrogen are fast and algal uptake of simple forms of DON such as amino acids may be immediate by algae and bacteria. Refractory organic nitrogen decay rates are much longer, but so are detention times in the Chesapeake. Dissolved conservative tracers are retained in the upper Bay on the order of months, and particulate organic nitrogen is estimated to be unlikely to be exported from the Chesapeake. Given these long detention times, organic nitrogen decay is likely to take place within the estuary, even for the most refractory of organic nitrogen. Even if the organic material is carried beyond the Chesapeake, the coastal waters beyond estuary boundaries have long detention times as well and the diagenesis of organic material here would be likely to contribute to coastal water eutrophication.

As a thought experiment, we could imagine some amount of completely refractory organic nitrogen released to tidal waters. Over time we would expect there would be a reservoir of this organic nitrogen in the water column or sediment, but this is not found. All that's found in

sediment cores of the Chesapeake are the “ashes” of a microbial pyre that have been buried in the sediment along with a trace of increasingly refractory organic nitrogen

Based on the above, no change is warranted in the NPDES approach used in the Chesapeake which bases nitrogen allocations on total nitrogen. The basis of this approach is the reasonable assumption that eventually in the riverine, estuarine, or coastal ocean system mineralization will occur. Of course, if any change were contemplated in this NPDES approach the allocations for all sources, including all nonpoint sources, would need to be recalculated on the same basis which is a level of effort equivalent to redoing the 2003 nutrient allocation process.

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